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(71) Applicant (*for all designated States except US*): EKA CHEMICALS AB [SE/SE]; S-445 80 Bohus (SE).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): GORZYNSKI, Marek, A. [DE/DE]; Am Courtenbachshof 3, D-52349 Düren (DE). MACHEREY, J., Heribert [DE/DE]; Altenweiher 15, D-52372 Kreuzau (DE).

(74) Agent: SCHÖLD, Zaid; Eka Chemicals AB, Patent Dept., P.O. Box 11556, S-100 61 Stockholm (SE).

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(57) Abstract

The invention relates to cationic polyurethanes and aqueous dispersions of cationic polyurethanes, their preparation and use as sizing agents in the making of paper. The invention further relates to hydroxy-functional quaternary ammonium compounds and compositions thereof, their preparation and use in the production of cationic polyurethanes.

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Quaternary ammonium compounds

The present invention generlly relates to quaternary ammonium compounds. More specifically, the invention relates to cationic polyurethanes and aqueous dispersions of cationic polyurethanes, their preparation and use in papermaking. The invention further relates to hydroxy-functional quaternary ammonium compounds and compositions thereof, their preparation and use in the production of cationic polyurethanes.

It is known in the papermaking art to use cationic polyurethanes (CPUR) as sizing agents in order to delay or prevent the absorption and spreading of aqueous solutions in sized paper products. Usually, CPUR's in the form of aqueous dispersions are used in surface sizing in which the sizing agent is applied to the paper surface at the size press.

U.S. Pat. No. 3,971,764 discloses high molecular weight CPUR sizing agents prepared by reacting a diol with a polyisocyanate to form a prepolymer with terminal isocyanate groups which is subsequently reacted with (a) a diol containing a tertiary nitrogen atom which is subsequently converted into the corresponding ammonium compound, or (b) a diol containing a nitrogen atom previously converted into the corresponding ammonium compound; method (a) being preferred. In these methods, the nitrogen atom can be rendered cationic by using an acid or alkylating agent and the patent discloses that hydrogen chloride, hydrochloric acid and dimethyl sulfate are useful for this purpose. Such CPUR dispersions generally provide good sizing response using low levels of sizing agent. It has, however, been observed that the CPUR dispersions exhibit stability problems and settling tendencies, in particular in the presence of electrolytes which are commonly added into the size press in order to prevent static electricity being built up during subsequent application, drying or converting processes. The insufficient stability may cause the CPUR particles contained in the dispersions to agglomerate and form deposits, leading to handling and application problems, deteriorated size performance and poorly sized paper.

According to the present invention it has been found that CPUR's having improved sizing and stability properties can be obtained by using in the polyurethane synthesis a hydroxy-functional quaternary ammonium compound (QUAT), i.e. an organic compound containing one or more hydroxyl groups and a positively charged quaternary nitrogen atom, in which the nitrogen has been quaternized with an epoxide. More specifically, the present invention relates to a method of producing a cationic polyurethane which comprises reacting a dihydroxy compound with a polyisocyanate to form a pre-polymer with terminal isocyanate groups which is then reacted with a hydroxy-functional quaternary ammonium compound containing a quaternary nitrogen that has a substituent derived from an epoxide. The invention thus relates to a method of producing cationic polyurethanes, to cationic polyurethanes per se and to their use, as further defined in the claims.

The method according to the present invention leads to high molecular weight CPUR's with outstanding properties. Aqueous dispersions of the present CPUR's exhibit improved stability and hereby the problems associated with prior art sizing dispersions based on CPUR can be reduced or overcome. The present CPUR dispersions further provide improved sizing which means that lower levels of sizing agent can be used to give the same sizing effect, thereby leading to cost reduction and economic benefits.

Dihydroxy compounds, or diols, that can be used as monomers in order to form the prepolymer, or intermediate product, according to the present invention include aliphatic and aromatic diols. The term "aliphatic", as used herein, refers to an essentially hydrocarbon structure apart from designated functional groups, which hydrocarbon structure may be interrupted by one or more heteroatoms, e.g. oxygen and nitrogen, and/or one or more groups containing heteroatoms, e.g. carbonyl and acyloxy groups. The term "aromatic", as used herein, refers to an aromatic, essentially hydrocarbon structure apart from designated functional groups, which hydrocarbon structure may be interrupted by one or more heteroatoms, e.g. oxygen and nitrogen, and/or one or more groups containing heteroatoms, e.g. carbonyl and acyloxy groups. It is generally preferred to use aliphatic diols and preferably such diols which have an aliphatic side-chain substituent which can contain from 1 to 30, suitably at least 5, preferably at least 10 and most preferably from 10 to 22 carbon atoms. The diols may be high molecular weight polymeric compounds such as polyester, polyether and polybutadiene diols, although it is generally more preferred to use non-polymeric aliphatic dihydroxy compounds which suitably contain from 2 to 20 and preferably from 2 to 10 carbon atoms in the chain connecting the two hydroxyl groups, i.e. in the main chain. Preferred aliphatic main chains include alkylenes and dialkyleneamines containing from 2 to 10 carbon atoms. Suitably the main chain is substituted with an aliphatic side-chain as described above; where the main chain contains a heteroatom which is nitrogen, it is preferred that the nitrogen carries the side-chain. Examples of suitable aliphatic dihydroxy compounds include ethylene and diethylene glycols, propane and butane diols, and higher molecular weight compounds such as fatty acid monoesters of triols such as glycerol and trimethylolpropane, e.g. glycerol monostearate and glycerol monobehenate, trimethylolpropane monostearate; oligomeric esterdiols such as diester diols, e.g. those obtained by reacting a dicarboxylic acid, e.g. adipic acid, with a molar excess of a diol, e.g. ethylene glycols; N-alkyl-diethanolamines, e.g. N-stearyl-diethanolamine; branched chain dihydroxy alkylenes, e.g. 1,2- and 1,4-dihydroxy-octadecanes. The higher molecular weight compounds are generally preferred, especially glycerol monostearate. Examples of aromatic diols that can be used include bisphenol A. Mixtures comprising one or more diols, such as any of those mentioned above, can also be used in the reaction with polyisocyanates.

Polyisocyanates that can be used as monomers to form the prepolymer in this method include aliphatic, aromatic and mixed aliphatic/aromatic compounds. Among the polyisocyanates, it is preferred to use diisocyanates. Where polyisocyanates containing more than two isocyanate groups are used, e.g. triisocyanates, it is preferred to admix them with diisocyanates. Generally, polyisocyanates are known in the art, for example as disclosed in Encyclopedia of Polymer Science and Engineering, Vol. 13, Second Ed., 1988, pp. 243-303, which is hereby incorporated herein by reference. Examples of suitable diisocyanates include toluene-2,4- and 2,6-diisocyanates, diphenylmethane-4,4'-diisocyanate, hexamethylene diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, cyclohexane-1,4-diisocyanate, isophorone diisocyanate and the like. It is also possible to use blocked isocyanates in known manner.

The reaction of the monomeric dihydroxy compound with the polyisocyanate can be carried out in conventional manner, for example as disclosed in U.S. Pat. No. 3,971,764, which is hereby incorporated herein by reference. As isocyanates are susceptible to nucleophilic attack and readily react with water, the prepolymer as well as the CPUR are preferably prepared in a reaction medium free from water and undesired nucloephiles. Suitably the reaction is carried out in a water-free inert organic solvent, e.g. acetone, optionally in the presence of a catalyst, e.g. diacetoxy-dibutyl-tin. The molar ratio of dihydroxy compound to polyisocyanate can be varied over a broad range and in most cases the molar ratio is within the range of from 1:1.1 to 1:3, suitably from 1:1.5 to 1:2.5 and preferably about 1:2. Preferably the hydroxyl- and isocyanate-containing reactants used in the first stage are uncharged which thus leads to an uncharged prepolymer.

The pre-polymer having terminal isocyanate groups obtained in the first stage of the method is then further reacted in a second stage with a hydroxyl-containing quaternary ammonium compound in order to introduce positive charges into the polyurethane. The second stage can be carried out generally as taught in U.S. Pat. No. 3,971,764 except that in the present method there is used a hydroxy-functional QUAT containing a quaternary nitrogen atom having a substituent derived from an epoxy-functional quaternizing agent. Suitable hydroxy-functional QUAT's include compounds obtained by reacting a tertiary amine, suitably a hydroxyl-containing tertiary amine; with an epoxide, e.g. an alkylene oxide such as ethylene oxide and propylene oxide or, suitably, a halogen-containing epoxide such as epihalohydrin, e.g. epichlorohydrin and epibromohydrin, preferably epichlorohydrin; and optionally with an acid. In a preferred embodiment of this invention, the hydroxy-functional QUAT is a compound containing one or more hydroxyl groups and a quaternary nitrogen atom having a substituent derived from a halogen-containing epoxide and having an anion derived from an acid.

Suitable QUAT's for use according to the invention can thus be represented by the general formula (I):

$$\begin{array}{ccccc} & & R_1 & & \\ & & | & & \\ R_2 & — & N^+ & — & R_4 \\ & & | & & \\ & & R_3 & & \end{array} \quad X^- \quad (I)$$

wherein R_1 and R_3 are each independently selected from aliphatic groups containing 1-10 and preferably 1-4 carbon atoms, which may be substituted with hydroxy, suitable at least one hydroxyl group is present in R_1 and/or R_3 and preferably R_1 and/or R_3 are linear or branched N-alkanols, e.g. N-ethanol; R_2 is an aliphatic group, suitably alkyl, containing 1-22 and preferably 1-4 carbon atoms, preferably methyl, ethyl, propyl or butyl; or alternatively R_1 and R_2 together with N form a linear or branched 5 to 7 membered ring, preferably aliphatic, which may be substituted with hydroxy and one or two carbon atoms may be substituted with NR_5R_6 in which R_5 and R_6 are aliphatic groups, preferably alkyl, containing 1-4 carbon atoms; R_4 is derived from an epoxide, e.g. an alkylene oxide such as ethylene oxide and propylene oxide, or, suitably, a halogen-containing epoxide, preferably epichlorohydrin; and X is an anion of an acid. In most cases, R_1, R_2, R_3 and N of the QUAT are derived from a tertiary amine. Generally, at least one hydroxyl group present in the QUAT is located on the substituent derived from the epoxide as quaternization of a tertiary amine by means of an epoxide normally leads to ring-opening of the epoxide group and formation of a hydroxyl group. Suitable QUAT's include those described in EP 541289 which is incorporated herein by reference for all purposes.

The R_4 substituent can thus be represented by the general formula (II) derived from an epoxide of the general formula (III):

$$\begin{array}{c} —R_7HC—\underset{\displaystyle \overset{|}{OH}}{CH}—R_8 \end{array} \quad (II) \qquad\qquad R_7HC—CH—R_8 \ \text{(with O bridging, } \backslash\ / \text{)} \quad (III)$$

wherein R_7 is hydrogen or an aliphatic group such as alkyl, preferably hydrogen; and R_8 is hydrogen or an aliphatic or aromatic group which can contain up to 20 carbon atoms, e.g. alkyl such as methyl, and which can be substituted with halogen; R_8 suitably being a halogen-containing aromatic or aliphatic group, preferably aliphatic, which may contain from 1 to 12 carbon atoms, preferably the halogen is chlorine and R_8 is $CH_2—Cl$. In addition, in QUAT's obtained by reacting a tertiary amine with an epoxide of formula (III) where $R_7 = H$ and $R_8 = H$ or alkyl such as methyl, i.e. an alkylene oxide, the R_4 substituent of the resulting QUAT of formula (I) may be a linear or branched hydrocarbon chain interrupted by one or more oxygen atoms, i.e. a di- or polyalkyleneoxy group, and containing a hydroxyl group, usually in

a terminal position, since the quaternization reaction may lead to di- or polyaddition of alkylene oxides.

The reaction between the prepolymer and QUAT, i.e. the reaction between isocyanate groups(s) of the prepolymer and hydroxyl group(s) of the QUAT, leads to chain-lengthening of the polyurethane. As will be appreciated, the degree of chain-lengthening depends on the number of reactive hydroxyl groups present in the QUAT where a mono-hydroxy-functional QUAT will act as a chain-terminator and thus provide less chain-lengthening. The QUAT used, e.g. the QUAT of formula (I), contains one or more hydroxyl groups and in most cases not more than 4 such groups, suitably from 1 to 3 hydroxyl groups and preferably 2 or 3. Mixtures containing more than one QUAT can of course be used. If desired, the QUAT can be used in combination with an additional hydroxy-functional compound, such as any of the hydroxylic compounds mentioned herein. In many cases, the use of admixtures containing QUAT and additional hydroxylic compound is preferred, for example where the QUAT exhibits limited solubility in the reaction medium used. Preferred additional hydroxylic compounds include the diols and hydroxy-functional tertiary amines described herein. In a preferred embodiment, use is made of a composition containing QUAT and a hydroxy-functional tertiary amine, suitably the same type of amine used to prepare the QUAT. The molar ratio of QUAT to additional hydroxylic compound, when used, can be varied over a broad range depending on, among other things, the isocyanate content in the prepolymer, the desired QUAT content and cationicity of the CPUR and the intended use of the CPUR. Usually, this molar ratio can be from 50:1 to 1:100. The molar ratio of hydroxyl groups to isocyanate groups in the second stage can be varied over a broad range and in most cases the molar ratio is within the range of from 1:0.5 to 1:2, suitably from 1:0.8 to 1:1.4 and preferably about 1:1.

The CPUR obtained may have an average molecular weight of at least 1,000, suitably at least 3,500 and preferably at least 4,000. The upper limit of molecular weight is not critical; usually it is about 30,000 and preferably about 15,000. After completed reaction the reaction mixture containing CPUR can be worked-up and converted into an aqueous dispersion in conventional manner, for example as disclosed in U.S. Pat. Nos. 3,971,764 and 4,617,341. Examples of useful steps include addition of acid, addition of water, evaporation of solvent and the like. In a preferred aspect of the process, an acid is added to accomplish neutralization by converting any tertiary nitrogen atoms present in the CPUR into the corresponding tertiary nitrogen acid addition salt.

The present invention further relates to an aqueous dispersion comprising the CPUR, to its use as a sizing agent in the making of paper and similar cellulose based products like board and paper board, wherein the aqueous CPUR dispersion is added to the

papermaking stock or applied to the surface of said products, preferably to surface size such products. The amount of CPUR dispersion added to the stock or applied to the surface of cellulosic products may be from 0.001 to 20% by weight, calculated as dry CPUR on dry cellulose based material and optional filler, suitably from 0.01 to 2% by weight. The CPUR dispersions may contain from about 1 to 50% by weight of CPUR, suitably from 5 to 25% by weight. The CPUR dispersions may of course be diluted with water prior to being used as sizing agents.

The present invention further relates to certain hydroxy-functional QUAT's. More specifically, the invention relates to quaternary ammonium compounds containing one or more hydroxyl groups and a quaternary nitrogen atom having a substituent derived from a halogen-containing epoxide and having an anion derived from an acid, compositions comprising such QUAT's, their preparation and use, as further defined in the claims.

The QUAT according to the invention, which contains a positively charged nitrogen attaching four radicals or substituents, can be represented by the general formula (I) defined above wherein R_4 is derived from a halogen-containing epoxide, preferably epichlorohydrin. The QUAT contains one or more hydroxyl groups and in most cases not more than 4 hydroxyl groups, preferably from 1 to 3 and more preferably 2 or 3 hydroxyl groups, which can be located on any of the substituents connected to the nitrogen.

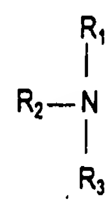
The anionic part of the QUAT of formula (I), i.e. X^-, is the anion of an acid; preferably a protonic acid such as HX, including organic acids, e.g. formic acid, acetic acid, propionic acid, methane sulfonic acid and p-toluene sulfonic acid, and inorganic acids, e.g. hydrogen halides and sulfuric acid. In a preferred embodiment, X is the anion of an organic acid and, in particular, formic acid.

Hydroxy-functional QUAT's of this invention can be prepared by reacting a tertiary amine with a halogen-containing epoxide in the presence of an acid. The reaction can be carried out using water as a solvent although it has been found, in accordance with the present invention, that hydroxy-functional QUAT's can be prepared in high yield in a very advantageous manner by reacting these reactants in the substantial absence of water. The method renders possible production of a wide range of hydroxy-functional QUAT's containing different N-substituents and counter-ions. Furthermore, after completed reaction, the reaction mixture obtained contains essentially no or very low amounts of oligomeric material and/or undesired by-products whereby the QUAT obtained can be used in the CPUR synthesis without costly purification. The QUAT obtained in the method also exhibit good stability. The subject method thus offers substantial technical and economic benefits.

Generally, it is common to use water as a solvent in the reaction and/or in the work-up when preparing quaternary ammonium compounds. Water, being a polar solvent,

normally favours the formation of charged reaction products like QUAT's and facilitates separation of the QUAT from the reaction mixture by means of extraction using water in conjunction with a water-immiscible solvent. However, monomers to be used in CPUR production should suitably be free from water since isocyanates are susceptible to nucleophilic attack. It has been experienced that extensively removing water from hydroxy-functional quaternary ammonium salts is complicated, costly and may lead to decomposition of the QUAT. Therefore, by providing a reaction which is carried out in the substantial absence of water, there is produced a QUAT especially useful for subsequent conversion with isocyanates into cationic polyurethanes.

The tertiary amine used in the present method is an organic compound containing at least one quaternizable tertiary nitrogen atom. Suitably the tertiary amine in an aliphatic amine. The tertiary amine suitably contain from 3 up to 25 carbon atoms, preferably from 4 to 10. Suitable tertiary amines can be represented the general formula (IV):



(IV)

wherein R_1, R_2, and R_3 are as defined above. The tertiary amine suitably contains from 0 to 3 hydroxyl groups and preferably 1 or 2 hydroxyl groups.

Examples of useful tertiary amines include non-hydroxylic amines such as N-trialkylamines, monohydroxy amines such as N,N-dialkyl alkanolamines, and dihydroxy amines such as N-alkandiol dialkylamines and N-alkyl dialkanolamines. Suitable tertiary amines include triethylamine, N,N-dimethyl stearylamine, N,N-dimethyl ethanolamine, 1,2-propanediol-3-dimethylamine, N-methyl diethanolamine, N-ethyl diethanolamine, N-propyl diethanolamine, N-n- and N-t-butyl diethanolamines, N-stearyl diethanolamine and N-methyl dipropanolamine. N-alkyl dialkanolamines and N,N-dialkyl alkanolamines, such as for example N-alkyl diethanolamines and N,N-dialkyl ethanolamines, in which the alkyl groups contain 1 to 4 carbon atoms are preferred, in particular N-methyl diethanolamine and N,N-dimethyl ethanolamine.

The epoxide in the present method is an organic compound capable of functioning as a quaternizing agent and contains at least one epoxide, or oxirane, group, and at least one halogen atom. Monoepoxy- and monohalogen-functional compounds are preferred. Suitable halogen-containing epoxides include compounds of the formula (III) defined above, preferably epichlorohydrin, which when being reacted

Suitable acids include protonic acids, HX, which forms the anion X^- of the QUAT. Preferably the acid is one that can be supplied as a substantially water-free acid. Examples of suitable acid include organic acids such as formic acid, acetic acid, propionic acid, methane sulfonic acid and p-toluene sulfonic acid as well as inorganic acids such as hydrogen chloride, hydrogen bromide and sulfuric acid. In a preferred embodiment of the invention, use is made of organic acids and, in particular, formic acid.

It has been found that the acid has an important role in the reaction and that higher levels of oligomeric material are usually formed when the reaction between the tertiary nitrogen and epoxide takes place in the absence of acid. When carrying out the reaction, the acid should suitably be present in an amount so that the reaction mixture has a pH of at least 7 and suitably a pH within the range of from 7 to 13. The pH of the reaction mixture can be measured in known manner, for example with a pH meter or pH electrode. It is preferred that at least part of the acid is present when bringing the amine into contact with the epoxide. Hereby the tertiary amine, or part thereof, may be present in the form of tertiary amine acid addition salt, e.g. $R_1R_2R_3N^+H\ X^-$, wherein R_1, R_2, R_3, and X are as defined above. In a preferred embodiment of the invention, the acid is intermittently or continuously fed to the reaction mixture so as to keep the pH within the desired range. Preferably, the pH value is between 7 and 12 and most preferably between 8 and 10.

In the method, the molar ratio of tertiary nitrogen to epoxide usually is at least 0.4:1, suitably at least 0.6:1, preferably at least 0.8:1. The upper limit for the molar ratio tertiary amine to epoxide can be high, for example 15:1 or higher, in many cases 10:1, usually 5:1, suitably 1.4:1 and preferably 1.2:1. In the method, the molar ratio of acid to epoxide can be varied over a broad range depending on, among other thing, the desired pH of the reaction mixture during the reaction. Suitably the reaction is carried out with the acid and epoxide in approximately equimolar amounts or with a molar excess of the acid. For instance, a molar excess of up to about 30% may be beneficial in terms of product stability.

The reaction can be carried out neat, i.e., in the absence of a solvent, or in the presence of a solvent. In a preferred aspect of the invention the reaction is carried out in the absence of inert organic solvents. Where solvents are used, it is preferred to use inert organic polar solvents. Suitable solvents include dimethylformamide, pyrrolidone, hexa-

The present method should be carried out in the substantial absence of water. Hereby is meant that the amount of water present during the reaction and work-up should be low, for example below 15% by weight, suitably below 5% by weight and preferably below 3% by weight, based on the weight of reactants. In a most preferred aspect of the invention, no water at all is present. The reaction can be run at a temperature below 50°C, suitably below 35°C and preferably below 25°C. The lower limit is not crucial and the reaction can be carried out at a temperature above -80°C, suitably above -25°C and preferably above 0°C. It may be advantageous to cool the reaction mixture during the reaction, especially when admixing the reactants.

In another aspect of this invention there is provided a method of producing a hydroxy-functional quaternary ammonium compound useful in the CPUR production which comprises reacting a tertiary amine with an epoxide in the presence of an acid and in the substantial absence of water and organic solvents. The tertiary amine and the acid can be as defined above and the epoxide is an organic compound capable of functioning as a quaternizing agent containing at least one epoxide, or oxirane, group, preferably having the general formula (III) above. The reaction is carried out in the substantial absence of water and organic solvents and hereby is meant that the amount of water and organic solvents, e.g. any of those defined above, should be low, for example in amounts defined above with respect to water but in this aspect meaning to the combined weight of water and organic solvent.

After completed reaction, the pH of the reaction mixture can be adjusted to 4-9 for the purpose of improving the stability of the QUAT, suitably to pH 5-8 and preferably to pH 6-7. This may be accomplished by means of any acid that is essentially water-free, e.g. any of those mentioned above. The solvent used in the reaction, if any, can be removed from the reaction mixture by evaporation, suitably at reduced pressure. The product formed can be used directly, for example in the production of CPUR's, without purification. If desired, the ammonium salt obtained may of course be subjected to any conventional purifiction step, e.g. extraction and crystallization in known manner.

The present method shows high selectivity and thus produces hydroxy-functional QUAT's in high yields with low or no formation of oligomeric and polymeric material. Furthermore, where epichlorohydrin is used as a quaternizing agent to produce the QUAT, low levels of unreacted epichlorohydrin and undesired by-products such as 1-chloro-2,3-propane diol (CPD) and 1,3-dichloro-2-propanol (DCP) are usually obtained. Generally, the conversion of epichlorohydrin to CPD is less than 5% and normally less than 3%, based on the weight of epichlorohydrin used in the reaction, and the conversion of epichlorohydrin to DCP is less than 1% and normally less than 0.1% by weight. Accordingly, one of the advantages of using the QUAT's of this invention in CPUR production is that CPUR's and

dispersions thereof can be provided with very low contents of unreacted halogen-containing epoxide, e.g. epichlorohydrin, and undesired by-products derived from the halogen-functional epoxide, e.g. CPD and DCP. In the CPUR's and CPUR dispersions according to the invention, the amount of halogen-containing epoxide such as epichlorohydrin present can be less than 10 ppm, suitably less than 5 and preferably less than 1 ppm, calculated as halogen-containing epoxide and based on CPUR solids, and the amount of halogenated by-products can be less than 1% by weight and suitably less than 0.5 % by weight, calculated as total amount of halogenated by-products and based on CPUR solids. Notably, when using epichlorohydrin, the CPD content can be less than 0.1% by weight, suitably less than 0.05% by weight and preferably less than 10 ppm, based on CPUR solids, and the DCP content can be less than 0.5% by weight, suitably less than 0.1% by weight and preferably less than 10 ppm, based on CPUR solids.

The invention further relates to a composition comprising the present hydroxy-functional quaternary ammonium compound, as further defined in the claims. The composition is substantially free from water, as defined above. In addition to the QUAT, the composition can for example contain unreacted starting materials such as any of those used in the reaction, e.g. any material used in excess, and minor amounts of reaction-typical by-products. The composition may also contain additional compounds admixed with the composition. Examples of such additional compounds include acids and tertiary amines, e.g. any of those defined herein. In a preferred embodiment, the QUAT is present in the composition in a predominant amount, based on weight, i.e., the weight ratio of QUAT to each of the other components present in the composition is higher than 1. In another preferred embodiment, a hydroxy-functional tertiary amine and/or its acid addition salt is present in the composition in a predominant amount, based on weight, preferably the tertiary amine. Such compositions are particularly useful in the preparation of CPUR. The tertiary amines and acids for formation of the acid addition salt may be any of those defined herein and suitably the same type of compounds used as reactants in the method of the invention.

The invention is further illustrated in the following Examples which, however, are not intended to limit same. Parts and percentages relate to parts by weight and percent by weight, respectively, unless otherwise stated.

Example 1

In accordance with the present invention, (3-chloro-2-hydroxypropyl)-bis(2-hydroxyethyl)-methylammonium formiate was prepared as follows:

To cooled 11.9 g (0.1 moles) of N-methyl diethanolamine, 98% concentrated formic acid was added with stirring to produce a pH of between 9 and 10, as measured b

a pH electrode. To this mixture was added 7.4 g (0.08 moles) of epichlorohydrin, and the reaction mixture was cooled so as to keep the temperature at 20°C, and additional formic acid was continuously added to keep the pH between 9 and 10. After stirring for 10 hours pH was adjusted to 6.5 by addition of formic acid. The desired product was formed in high yield, as shown by ^{13}C-NMR and GPC, and the formation of by-products was low. Essentially no oligomeric and polymeric material was formed. The product so obtained was stable for more than three months at room temterature.

Example 2

The procedure of Example 1 was followed except that the amine used was N,N-dimethylethanolamine and that the amine and epichlorohydrin were used in equimolar amounts. The desired product, (3-chloro-2-hydroxypropyl)-(2-hydroxyethyl)-dimethyl-ammonium formiate, was obtained in high yield. Only minor amounts of impurities were formed and there were essentially no formation of oligomeric and polymeric material.

Example 3 (Comparison)

The procedure of Example 1 was followed except that no acid was used in the method. An exothermic reaction between N-methyl diethanolamine and epichlorohydrin took place which was very difficult to control and phase separation was observed, indicating formation of oligomeric/polymeric material. After two days the reaction mixture had been completely converted to a solid mass and no monomeric compounds could be detected.

Example 4

A cationic polyurethane according to the invention was prepared as follows:

To a solution of 18.3 g of glycerol monostearate and 18.3 g of toluene diisocyanate in 50 g of water-free acetone at a temperature of 40°C was added 17 mg of dibutyl tin-diacetate in acetone. The solution was refluxed for 1 hour under vigorous stirring. A sample of the solution was taken away for determination of residual NCO-groups and showed a residue of 14%. A mixture of 5.1 g of N-methyl diethanolamine (N-MDEA) and 2.2 g of QUAT according to Example 1, where the mixture had a molar ratio N-MDEA to QUAT of 5:1, was added to the solution at 50°C followed by addition of further 50 ml of acetone. The mixture was refluxed for 1 hour and then 40 ml of 1 M HCl was added for neutralization and formation of tertiary amine acid addition salt and then the mixture was diluted with 250 ml of water. Acetone was evaporated under reduced pressure at 60-70°C to afford a clear residue in the form of a dispersion containing approximately 15-17% of CPUR at pH 4. The contents of epichlorohydrin, CPD and DCP were all below the detection limit of the gas chromatographic

method used; the epichlorohydrin content was below 1 ppm, the CPD and DCP contents were both below 10 ppm.

Example 5

A cationic polyurethane according to the invention was prepared as in Example 4 except that the molar ratio of N-MDEA to QUAT was 4:1.

Example 6

A cationic polyurethane according to the invention was prepared as in Example 4 except that the molar ratio of N-MDEA to QUAT was 3:1 which thus corresponded to about 25% quaternization of the nitrogen atoms.

Example 7 (Comparison)

In this test, a CPUR was prepared by reacting HCl with a polyurethane containing tertiary amine groups.

Glycerol monostearate was reacted with toluene diisocyanate as in Example 2 and then the pre-polymer with terminal NCO-groups was reacted with solely N-methyl diethanolamine. The uncharged polyurethane was rendered cationic by addition of 1 M HCl which converted tertiary nitrogen atoms into the corresponding acid addition salt. Work-up was made as in Example 4 which yielded a dispersion containing about 15-16% of CPUR at pH 4.

Example 8 (Comparison)

The procedure of Example 7 was followed up to the reaction with N-methyl diethanolamine. The polyurethane so formed was reacted with dimethyl sulfate to effect quaternization of about 25% of the nitrogen atoms and then 1 M HCl was added for neutralization. The work-up was carried out as in Exampl 4 which resulted in a dispersion containing about 15% of CPUR at pH 4.

Example 9

Stability of the cationic polyurethane dispersions of Examples 4-8 was evaluated by adding a saturated aqueous solution of sodium sulfate to 100 ml of aqueous dispersion

Table I

Na_2SO_4(aq.) added (ml)	Appearance of Cationic Polyurethane Dispersion				
	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8
0	Clear	Clear	Clear	Clear	Clear
1.0	Clear	Clear	Clear	Precip	Clear
2.0	Clear	Clear	Clear	Precip	S-Turb
3.0	Clear	Clear	Clear	Precip	S-Turb
4.0	-	-	S-Turb	-	V-Turb
5.0	-	-	S-Turb	-	Precip

wherein S-Turb = slightly turbid
V-Turb = very turbid
Precip = precipitation
\- = not analyzed

As is evident from Table I, the dispersions of cationic polyurethane of Examples 4-6 according to the invention were considerably more stable than the polyurethane dispersions used for comparison purposes.

Example 10

Sizing efficiency of the CPUR dispersions according to Examples 4-7 was evaluated by means of the Cobb Test, using German DIN standard 53/32, which is conventional in the art. The Cobb-values correspond to paper absorption of water, expressed in g/m^2 of water take-up after contact for 1 minute. The values measured on the sized paper sheets are set forth in Table II, where dosage (%) refers to dry cationic polyurethane on dry sheet.

Table II

Sizing agent dosage (%)	Cobb-value obtained using Polyurethane Sizing Dispersion			
	Ex. 4	Ex. 5	Ex. 6	Ex. 7
0.075	80	80	74	-
0.10	40	36	36	74
0.15	22	21	23	29
0.20	-	-	-	22

As can be seen from Table II, the sizing agents of Examples 4 to 6 according to the

Claims

1. A method of producing a cationic polyurethane, c h a r a c t e r i s e d in that it comprises

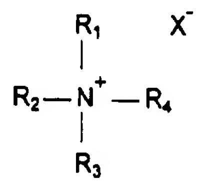
(a) reacting a dihydroxy compound with a polyisocyanate to form a pre-polymer having terminal isocyanate groups;

(b) reacting the pre-polymer with a hydroxy-functional quaternary ammonium compound containing a quaternary nitrogen having a substituent derived from an epoxide.

2. A method according to claim 1, c h a r a c t e r i s e d in that the hydroxy-functional quaternary ammonium compound contains a quaternary nitrogen having a substituent derived from a halogen-containing epoxide.

3. A method according to claim 1 or 2, c h a r a c t e r i s e d in that the quaternary ammonium compound contains from 1 to 3 hydroxyl groups and a quaternary nitrogen having a substituent derived from epichlorohydrin and has an anion derived from an acid.

4. A method according to claim 1, 2 or 3, c h a r a c t e r i s e d in that the quaternary ammonium compound has general formula (I):



(I)

wherein R_1 and R_3 independently are selected from aliphatic groups containing 1-4 carbon atoms which may be substituted with hydroxy, at least one hydroxyl group being present in R_1 and/or R_3; R_2 is an alkyl group containing 1-4 carbon atoms; R_4 is derived from epichlorohydrin and X is an anion of an acid.

5. A method according to claim 1, 2, 3 or 4, c h a r a c t e r i s e d in that the quaternary ammonium compound has an anion of an organic acid.

6. A method according to any of the preceding claims, c h a r a c t e r i s e d in that the dihydroxy compound comprises an aliphatic compound substituted with an aliphatic side-chain containing at least 5 carbon atoms.

7. A method according to any of the preceding claims, c h a r a c t e r i s e d in that the dihydroxy compound comprises an aliphatic compound containing from 2 to 10 carbon atoms in a main chain connecting the two hydroxyl groups, the main chain being substituted with an aliphatic side-chain containing at least 10 carbon atoms.

8. A method according to any of the preceding claims, c h a r a c t e r i s e d in that the polyisocyanate comprises toluene diisocyanate.

9. A method according to any of the preceding claims, characterised in that the cationic polyurethane formed has a molecular weight of at least 3500.

10. A cationic polyurethane obtainable by a method according to any of claims 1 to 9.

11. An aqueous dispersion comprising a cationic polyurethane according to claim 10.

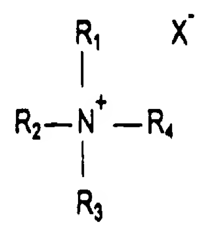
12. An aqueous dispersion according to claim 11, characterised in that the content of epichlorohydrin is less than 10 ppm, based on cationic polyurethane solids.

13. An aqueous dispersion according to claim 11 or 12, characterised in that the content of 1-chloro-2,3-propane diol (CPD) is less than 0.05% by weight, based on cationic polyurethane solids, and the content of 1,3-dichloro-2-propanol (DCP) is less than 0.1% by weight, based on cationic polyurethane solids.

14. Use of an aqueous dispersion comprising a cationic polyurethane according to claim 11, 12 or 13 as a sizing agent for cellulose based products.

15. A hydroxy-functional quaternary ammonium compound containing one or more hydroxyl groups and a quaternary nitrogen having a substituent derived from a halogen-containing epoxide and having an anion derived from an acid, with the proviso that the anion is not chloride.

16. A quaternary ammonium compound according to claim 15 having the general formula (I):



(I)

wherein R_1 and R_3 independently are selected from aliphatic groups containing 1-4 carbon atoms which may be substituted with hydroxy, at least one hydroxyl group being present in R_1 and/or R_3; R_2 is an alkyl group containing 1-4 carbon atoms; R_4 is derived from epichlorohydrin and X is an anion of an acid.

17. A quaternary ammonium compound according to claim 15 or 16 having an anion of an organic acid.

19. A composition according to claim 18, characterised in that the hydroxyl-containing tertiary amine and/or acid addition salt thereof is present in a predominant amount, based on weight.

20. A method of producing a hydroxy-functional quaternary ammonium compound by reacting a tertiary amine with a halogen-containing epoxide in the presence of an acid and in the substantial absence of water.

21. A method of producing a hydroxy-functional quaternary ammonium compound by reacting a tertiary amine with an epoxide in the presence of an acid and in the substantial absence of water and organic solvents.

22. A method according to claim 20 or 21, characterised in that the tertiary amine being reacted with the epoxide and the acid is N-alkyl diethanolamine or N,N-dialkyl ethanolamine in which the alkyl groups contains from 1 to 4 carbon atoms.

23. A method according to claim 20, 21 or 22, characterised in that that the acid is formic acid, acetic acid, propionic acid, methane sulfonic acid, p-toluene sulfonic acid, hydrogen chloride, hydrogen bromide or sulfuric acid.

24. A method according to any of claims 20 to 23, characterised in that that the epoxide is epichlorohydrin.

25. A method according to any of claims 20 to 23, characterised in that that the epoxide is ethylene oxide or propylene oxide.

26. A method according to any of claims 20 to 25, characterised in that at least part of the acid is present when bringing the amine into contact with the epoxide and that additional acid is intermittently or continuously fed to the reaction mixture during the reaction.

27. Use of a hydroxy-functional quaternary ammonium compound according to any of claims 15 to 17 or a composition comprising a hydroxy-functional quaternary ammonium compound according to claim 18 or 19 for the production of a cationic polyurethane.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 97/00873

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C07C 215/40, C08G 18/08
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C07C, C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0541289 A1 (WITCO CORPORATION), 12 May 1993 (12.05.93) --	1-27
A	GB 1491091 A (AKZO NV), 9 November 1977 (09.11.77) -- --------	1-27

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" erlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 Sept 1997	11 -09- 1997

Name and mailing address of the ISA/	Authorized officer
Sw dish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Dagmar Järvman Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT
Information on patent family members

06/08/97

International application No.
PCT/SE 97/00873

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